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ON THE EQUILIBRIUM STRUCTURE OF SIMPLE LIQUIDS*

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ABSTRACT

It is shown that the repulsive (not merely the positive)
portion of the Lennard-Jones potential quantitatively dominates
the equilibrium structure of the Lennard-Jones liquid. A simple
and accurate approximation for the radial distribution function at
high densities is presented.

It is often remarked that the repulsive forces in a simple liquid play an important role in forming the equilibrium structure of such a fluid.[1,2,3] By studying the spectrum (Fourier transform) of the two-particle correlation function,

$$\hat{h}(k) = \rho \int [g(r)-1]\bar{e}^{\,i\underline{k}\cdot\underline{r}}\, d\underline{r} \tag{1}$$

where $g(r)$ is the usual radial distribution function and ρ is the average number density, we are able to formulate this idea in a precise and useful way.

In order that a convenient basis for comparison be available, the Lennard-Jones fluid is considered: a classical N-particle system in which the total potential energy is a sum of the Lennard-Jones pair potentials, $w(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$. Our attention is focused on $\hat{h}(k)$ for the Lennard-Jones liquid. In particular, for liquid densities ($\rho\sigma^{3}\gtrsim.4$) we hypothesize and then verify the following statements: 1. <u>At intermediate and large wave-vectors ($k\sigma\gtrsim\pi$), the quantitative behavior of $\hat{h}(k)$ is dominated by the repulsive forces</u> (the attractive forces are primarily manifested in the small wave-vector portion of the spectrum); 2. <u>For high densities ($\rho\sigma^{3}\gtrsim.65$) the behavior of $\hat{h}(k)$ even at small wave-vectors ($k\sigma\lesssim\pi$) is at least qualitatively determined by the repulsive forces</u>. Physically, the first statement is understood once it is recalled that $\hat{h}(k) + 1$ represents the linear response of the fluid structure to a disturbance of wavelength $2\pi/k$.[4] While a short wavelength disturbance will probe both the repulsive and attractice forces in a fluid, it is reasonable that the presence of the harsh repulsions, rather than the slowly varying longer ranged attractions, will dominate the response of the fluid to such a disturbance. The second

statement is equivalent to asserting that the correlations in a simple liquid are almost entirely due to excluded volume effects when the density is high. While this latter part of our hypothesis has been stated quali- tatively by many authors,[1,2,3] its quantitative validity has not been appreciated.

To see how the repulsive portion of the pair-potential affects the liquid structure, it is convenient to consider a reference system in which the pair-potential, $u_o(r)$, contains all the repulsive forces implied by the Lennard-Jones potential, $w(r)$, and no attractive forces. With the additional condition that the reference system has a well defined thermodynamic limit, $u_o(r)$ is defined uniquely:

$$\left.\begin{array}{ll} u_o(r) = w(r) + \epsilon, & r<2^{1/6}\sigma \\ \\ = o & , r\geq 2^{1/6}\sigma \end{array}\right\} \tag{2}$$

It should be noted that the repulsive part of $w(r)$ is the portion with negative slope and not the portion which is merely positive. In terms of the radial distribution function for the reference system, $g_o(r)$, and its spectrum, $\hat{h}_o(k)$, the hypothesis stated above can be expressed as follows: At all liquid densities, the approximation $\hat{h}_o(k) = \hat{h}(k)$ is very accurate for $k\sigma \geq \pi$; at high densities ($\rho\sigma^3 \geq .65$), $g(r)$ closely resembles $g_o(r)$. Thus, the task of verifying our hypothesis is reduced to determining $g_o(r)$ and $\hat{h}_o(k)$. Rather than perform expensive machine calculations to obtain this information, we have invented an approximation method to describe the reference system. Tests have been performed[5] which indicate that our treatment is certainly

accurate enough for the purposes of this work. To discuss the method, we introduce the function $y_o(r)$ which is defined by the equation

$$g_o(r) = y_o(r)\exp[-\beta u_o(r)] \tag{3}$$

where β is the reciprocal of Boltzmann's constant times the temperature. Physically, $y_o(r)$ gives the correlations that exist in the reference system beyond the range of the reference interaction, $u_o(r)$. Since this interaction is harshly repulsive, it seems probable that $y_o(r)$ can be approximated by the similar function appropriate to a hard-sphere system of diameter d, $y_d(r)$. For this reason, we consider the following approximation:

$$g_o(r) \simeq y_d(r)\exp[-\beta u_o(r)] \tag{4}$$

or

$$\hat{h}_o(k) \simeq \hat{h}_d(k) + \rho \int d\underline{r}\, y_d(r)\left(e^{-\beta u_o} - e^{-\beta u_d}\right)e^{-i\underline{k}\cdot\underline{r}} \tag{4'}$$

where $\hat{h}_d(k)$ denotes the spectrum for the hard-sphere system of diameter d, and u_d denotes a hard-core repulsion of diameter d. By recalling $\hat{h}_o(k)$'s role as a linear response function, it is seen that Eq. (4) is equivalent to assuming that for intermediate and long wavelength disturbances, the response of the reference system is accurately given by the response of a hard-sphere system. Thus, by equating the long wavelength (small k) responses of the reference and hard-sphere systems, we have a physically reasonable density and temperature dependent criterion for determining d:

$$\int d\underline{r}\,\left(y_d\, e^{-\beta u_o} -1\right) = \int d\underline{r}\,\left(y_d e^{-\beta u_d} -1\right) \tag{5}$$

Finally, for lack of better analytic or extensively tabulated hard-sphere functions, we use the analytic solution of the Percus-Yevick equation to give us $\hat{h}_d(k)$ and $y_d(r)$ (o<r<2d).[6] Though it is fairly accurate, it represents our major source of error in the computations reported below.

When Eq. 5 is solved for $d(\beta,\rho)$ and plotted along several isochores, graphs are obtained[5] that are very similar to those given by Verlet (Fig. 17, Ref. 1) for the effective hard-sphere diameter needed to empirically "fit" a hard-sphere spectrum, $\hat{h}_d(k)$, to the Lennard-Jones spectrum, $\hat{h}(k)$, at intermediate wave-vectors. Thus, we believe Verlet was observing the behavior we have hypothesized: for $k\sigma \gtrsim \pi$, the spectrum is dominated by the repulsive (reference) forces. In Fig. 1, we plot $\hat{h}_o(k)$ (as obtained from our treatment of the reference system) at two thermodynamic states, (labeled I and II) and compare with Verlet's molecular dynamics results.[1] For state I, the density is sufficiently low to illustrate the dramatic discrepancy and then similarity between $\hat{h}_o(k)$ and the true Lennard-Jones spectrum as we pass from small to large wave-vectors. Incidently, for state I, the value of d obtained from Eq. 5 is $(1.005)\sigma$; Verlet reports a hard-sphere model d of $(1.0)\sigma$. From the curve for state II, we see that at high densities, the excluded volume effects dominate the correlations to such an extent that $\hat{h}_o(k)$ is also in good agreement with the Lennard-Jones spectrum for small wave-vectors. The value of d for this thermodynamic state is $(1.025)\sigma$; Verlet's hard-sphere model d is $(1.026)\sigma$.

The agreement between $\hat{h}_o(k)$ and $\hat{h}(k)$ that is observed at high densities implies that $g_o(r)$ should closely resemble $g(r)$ (except for very large r) at high densities. In Fig. 2 a plot of $g_o(r)$ as described in Eq. 4 is compared

with "exact" Lennard-Jones $g(r)$;[1] the thermodynamic state is similar to state II in Fig. 1. The agreement between $g_o(r)$ and $g(r)$ is excellent. To emphasize how accurate it is, we have also plotted the $g(r)$ obtained by solving the Percus-Yevick equation for the Lennard-Jones fluid.[6a,7] We mention that the Fourier inversion of $\hat{h}_o(k)$ at a moderate density (e.g. the thermodynamic state I considered in Fig. 1) agrees poorly with the Lennard-Jones $g(r)$ for all r.[5] This behavior is a manifestation of the discrepancy between $\hat{h}_o(k)$ and $\hat{h}(k)$ for small k. It emphasizes the convenience of considering the spectral representation of the structure rather than $g(r)$ itself. While the attractive forces appreciably contribute to only a small part of the spectrum, $k\sigma \lesssim \pi$, the attractions and repulsions contribute (at low and moderate densities) to $g(r)$ for all $r \gtrsim \sigma$. Thus, it is difficult to say what type of interaction produces a certain effect in $g(r)$. Our results indicate that this difficulty is not encountered when the spectrum is considered.

Finally, as a further check on the accuracy of the approximation $g_o(r) = g(r)$ at high densities we replace $g(r)$ by $g_o(r)$ in the pressure (virial) equation

$$\beta p/\rho = 1 + (\beta\rho/6)\int r(\partial w(r)/\partial r)g(r)d\underline{r} \tag{6}$$

and in the energy equation for the excess internal energy

$$\beta\Delta E/N = (\beta\rho/2)\int w(r)g(r)d\underline{r} \tag{7}$$

Once again, the calculations were performed within the context of our approximate treatment of the reference system. A few of our results are

presented in Table I and compared with those obtained from molecular dynamics[8] and the numerical solution of the Percus-Yevick equation for the Lennard-Jones system.[7] These results are representative of those found when a far more extensive comparison with molecular dynamics is made at several high densities $(\rho\sigma^3 \geq .65)$.[5]

It is our opinion that we have demonstrated the validity of the hypothesis stated at the beginning of this report. In so doing we have also discovered a very simple and accurate theory for the structure of dense liquids: namely the approximation $g(r) \simeq g_0(r)$ combined with Eq. 4. In a future publication,[5] our ideas will be documented more thoroughly. At that time we will also discuss, in detail, the relevance of our hypothesis to perturbation theories for liquids.[2]

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Table I. Approximate and molecular dynamics results for the pressure
and internal energy as obtained from Eqs. 6 and 7 respectively.
Columns 3 and 6 give the values found by applying the approxi-
mation $g_o(r) \simeq g(r)$. Columns 4 and 7 give the molecular
dynamics results (Ref. 8); the error bounds here are ±.05.
The results obtained by using the solution of the Percus-
Yevick equation for $g(r)$ (Ref. 7) are given in columns 5
and 8.

Thermodynamic State		$\beta p/\rho$			$-\beta\Delta E/N$		
$\rho\sigma^3$	$(\beta\varepsilon)^{-1}$	This Work	MD	PY	This Work	MD	PY
.85	.88	1.82	1.64	3.17	6.77	6.75	6.61
.85	.786	1.23	.99	2.97	7.70	7.70	7.51
.85	.719	.69	.36*	2.82	8.52	8.51	8.28
.85	1.128	2.82	2.78	3.57	5.08	5.05	4.98

* Molecular dynamics results for $\rho\sigma^3$=.85, $(\beta\varepsilon)^{-1}$=.72, predict
$\beta p/\rho$=.43 (Ref. 8).

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FIGURE CAPTIONS

Fig. 1. Plots of $\hat{h}(k)$ for two thermodynamic states: state I is $\rho\sigma^3$=.5426, $(\beta\epsilon)^{-1}$=.1.326; state II is $\rho\sigma^3$=.844, $(\beta\epsilon)^{-1}$=.723. The lines represent Eq. 4'; the circles and triangles denote the molecular dynamics results (Ref. 1) for states I and II respectively.

Fig. 2. Plots of $g(r)$ at a high density: $\rho\sigma^3$=.85, $(\beta\epsilon)^{-1}$=.88. The line represents the approximation $g_0(r) \simeq g(r)$; the circles are molecular dynamics results (Ref. 1); the dashed line represents the numerical solution of the Percus-Yevick equation for the Lennard-Jones potential (Ref. 7).
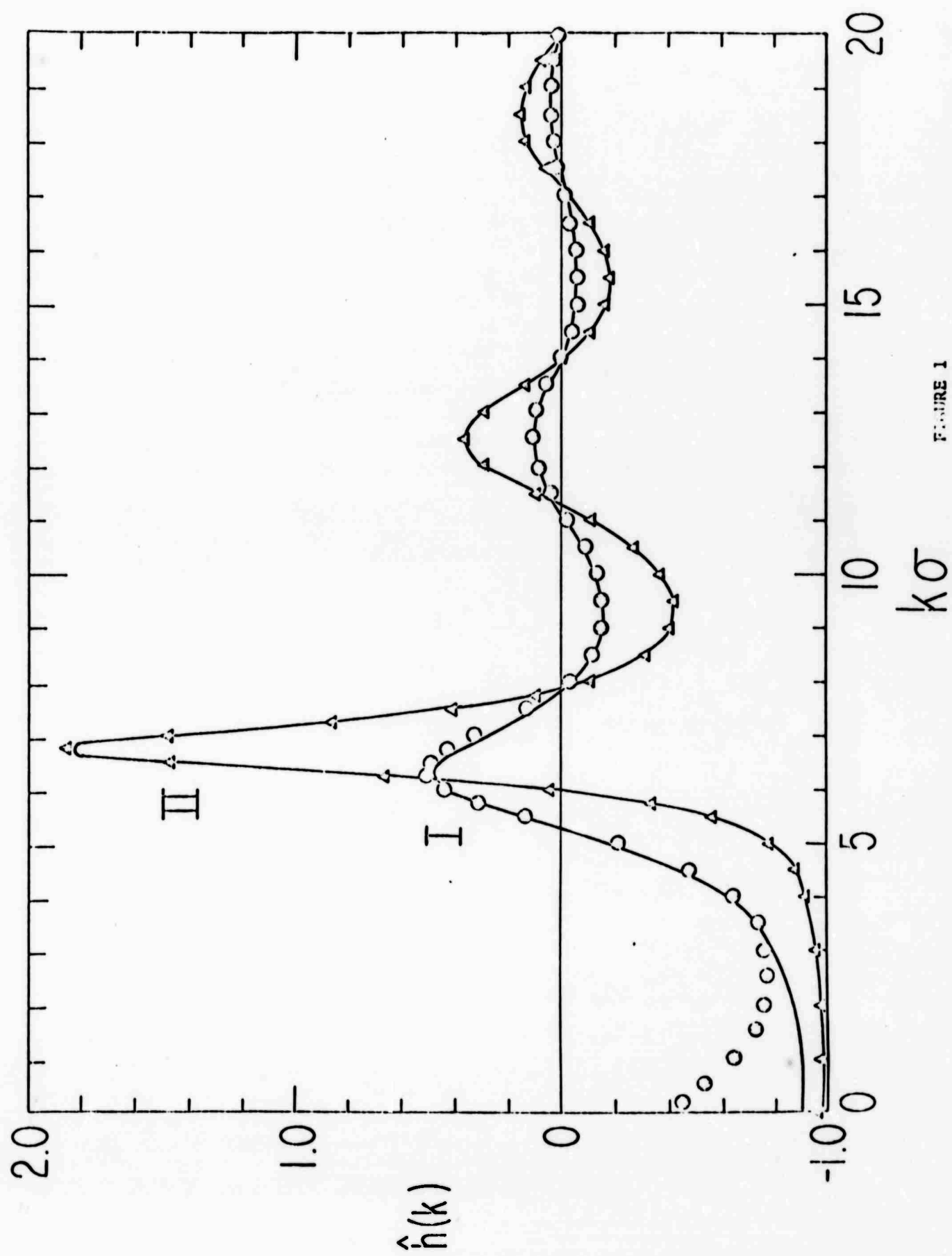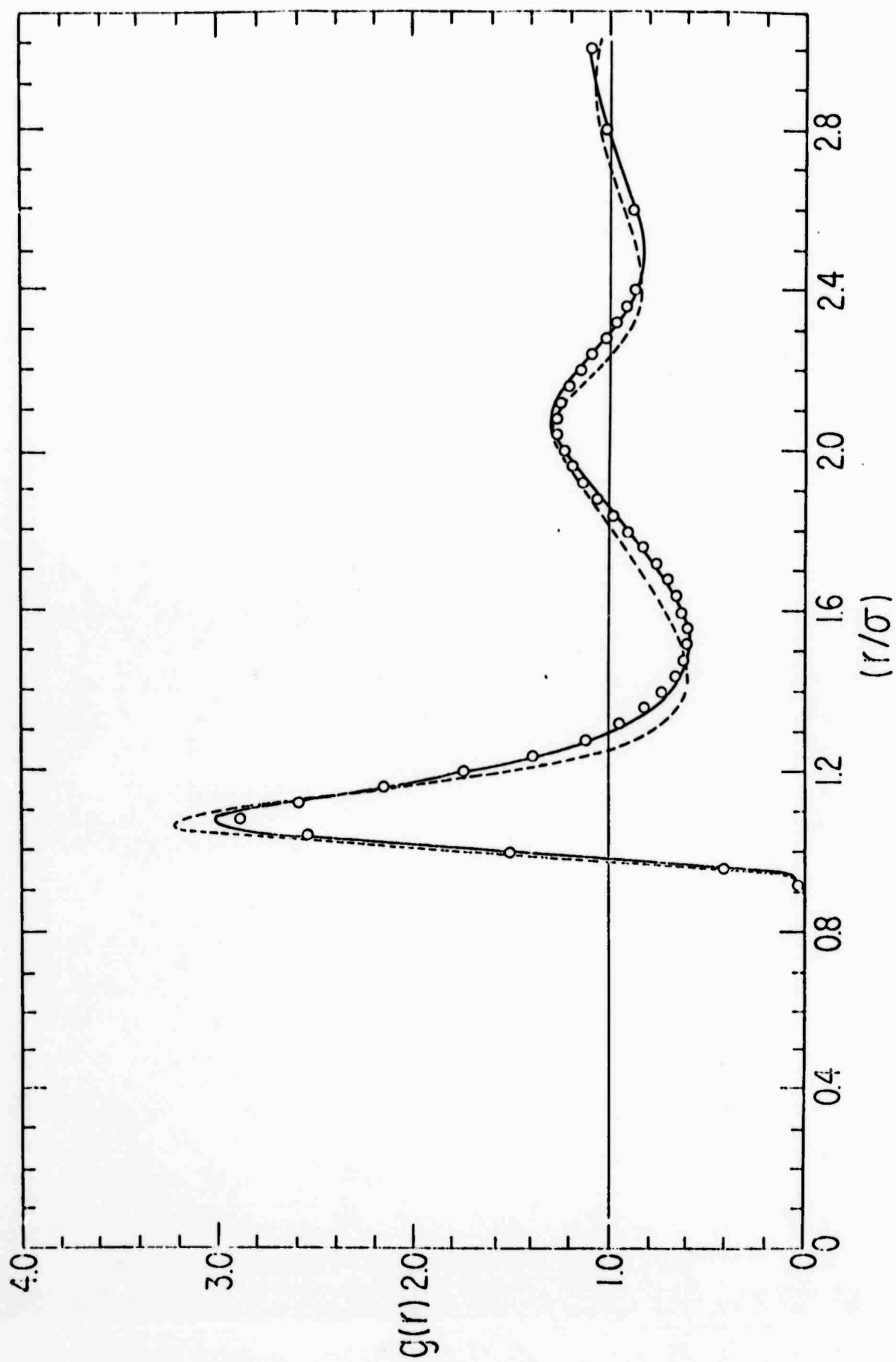
FIGURE 1

FIGURE 2

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13. ABSTRACT

It is shown that the repulsive (not merely the positive) portion of the Lennard-Jones potential quantitatively dominates the equilibrium structure of the Lennard-Jones liquid. A simple and accurate approximation for the radial distribution function at high densities is presented.

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